

Natural radioactivity and elemental composition of beach sands in the Calabria region, south of Italy

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Abstract A comprehensive study was conducted to determine the natural radioactivity concentrations and the geological provenience of beach sand samples from twelve different sites of the coast of Calabria, south of Italy, a popular tourist destination especially in summer. The radioactivity investigation was performed by using high resolution gamma-ray spectrometry. From the measured gamma-spectra, the average activity concentrations were determined for ^{226}Ra , ^{232}Th and ^{40}K for a depth of 5–20 cm. Results of this study were compared to values from other locations around the world. The corresponding radiation hazards were also estimated. X-ray fluorescence spectrometry (XRF) measurements were performed for the quantitative elemental analysis of the sands, revealing the major and minor elements present in the investigated samples. From XRF experimental results it was possible to estimate the geological provenience of the analyzed sands. These data record the radioactivity background levels in beach sands and could be used as reference information.

Keywords Environmental radioactivity · Radiological risk · Sand · Gamma spectrometry · X-ray fluorescence spectrometry

Introduction

Natural radioactivity provides the greatest contribution to the dose received by the population. From this point of view important radionuclides are those belonging to the radioactive families ^{238}U , ^{232}Th and ^{40}K (UNSCEAR 1993, 2000). These radionuclides and their product of decay are commonly found in different concentrations in environmental matrices, in particular in water, rocks and soils (Navas et al. 2002). The chemical composition and the natural radioisotopes activity concentration in the soil widely vary with the geomorphological and the geographical features of the investigated site (Srilatha et al. 2015). In particular sand deposits are the result of erosion and weathering of metamorphic and igneous rocks. In the latter the highest levels of natural radionuclides are found. The study of the activity concentration of natural radionuclides in sands allowed us to evaluate the radiological risk due to the external gamma radiation exposure for individuals who spend their holidays in these beaches.

In this article beach sands from the coast of Calabria, south of Italy, were analyzed to identify and quantify natural gamma-emitting radionuclides. For this purpose, HPGe gamma spectrometry was used to investigate about ^{226}Ra , ^{232}Th and ^{40}K activity concentration to record the radioactivity background levels.

X-ray fluorescence spectrometry (XRF) was employed for the quantitative elemental analysis of the sands and to determine their geological provenience.

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Materials and methods

In situ radiometric analysis

The environment dose rate measurements were performed at a height of 1 m above the ground level by using a pressurized ion chamber detector, THERMO FHT 191 N, 10 nSv/h–10 Sv/h dose rate range, 35 keV–7 MeV energy range (THERMO FHT 191 N user manual 2008). All readings in the beaches were in the sand area through a transect which covers the area of interest. The number of readings taken at each beach is directly related to the size of the sand beach area. Ten readings of 10 min each were taken at each point of the transect and the average was recorded.

Sand sampling and preparation

All sand samples were collected from the spot showing highest gamma dose rate determined by in situ measurement, for a depth of 5–20 cm. Ten samples, around 1 kg each, were collected for each of the twelve selected locations of the coast of Calabria, south of Italy, as indicated in Fig. 1.

Samples were collected with a metal sampler and stored into labeled plastic boxes. All samples were dried at 105° C in an oven, sieved to obtain a particle size less than 2 mm and successfully inserted in Marinelli hermetically sealed containers of 1 L capacity. After 40 days, the secular radioactive equilibrium between ^{226}Ra and their daughter products was attained and samples were ready for gamma spectrometry counting.

For non-destructive energy dispersive X-ray fluorescence spectrometric measurements 9 g of finely powdered sand mixed with 2.6 g of wax were employed for each investigated sample. They were placed in a 15 tons press for 90 s to obtain a square tablet, subsequently analyzed by XRF.

Gamma spectrometry analysis

In the gamma spectrometry measurements samples were counted for a time equal to 70,000 s and ^{226}Ra , ^{232}Th and ^{40}K activity concentration were determined. The 295.21 and 351.92 keV ^{214}Pb and 1120.29 keV ^{214}Bi gamma ray lines were used to determine the ^{226}Ra activity concentration. The ^{232}Th activity concentration was determined by using the 911.21 and 968.97 keV ^{228}Ac γ -lines, while for ^{40}K the evaluation was performed from its γ -line at 1460.8 keV. The uncertainty is given at the 95 % confidence level. The instrumentation used for the analysis consists of two Ortec high purity germanium detectors

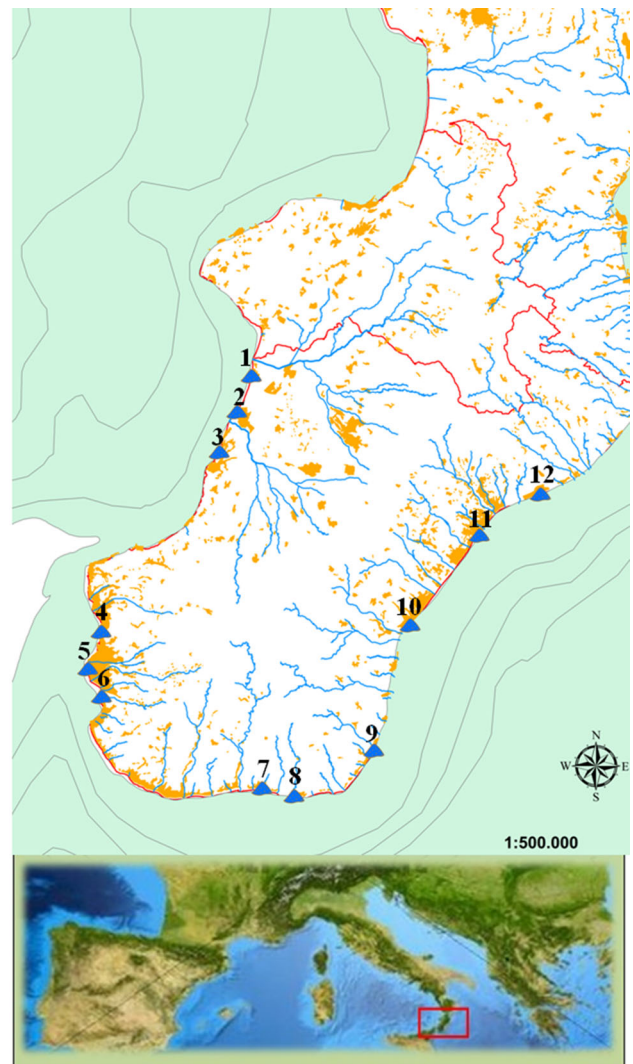


Fig. 1 Map of the investigated region. The *yellow areas* indicate the population density

(HPGe), electrically cooled, with integrated digital electronics. The first detector is a reverse biased semiconductor (GMX) having a FWHM resolution of 1.94 keV, relative efficiency at the reference peak (^{60}Co at 1.33 MeV) of 37.5 % and peak to Compton ratio of 65:1. The second detector is a direct biased semiconductor (GEM), characterized by a FWHM resolution of 1.85 keV, relative efficiency of 40 % and peak to Compton ratio of 64:1. Detectors are placed inside lead wells to shield the background radiation environment. The measurement systems have previously been calibrated with respect to the investigated gamma radiation energy and to the detection efficiency. All these operations were performed using a multi peak Marinelli geometry gamma source (SV 277) of 1 L capacity, covering the energy range 59.54 keV (^{241}Am)–1836 keV (^{88}Y). The verification of the detector

parameters (relative efficiency, resolution and peak to Compton ratio) was performed using a ⁶⁰Co point source placed at 25 cm from the detectors. The analysis was performed using the software Ortec Gamma Vision (Ortec Gamma Vision-32 v. 6 2010).

The quantitative analysis of the gamma spectrum consists of the following steps: identification of emitted gamma peaks, whose net area meets the default statistical threshold; background subtraction; attribution of identified gamma lines to radionuclides present in the library of analysis; efficiency correction and calculation of activity and measurement uncertainties; activity correction for self-absorption; calculation of the detection limit; production of analysis reports (Sima 1992).

The activity concentration of each identified radionuclide is calculated using the following formula:

$$c = \frac{N_E}{\varepsilon E t \gamma_d M} \tag{1}$$

where N_E indicates the net area of a peak at energy E , ε and γ are the efficiency and yield of the photopeak at energy E , respectively, M is the mass sample (kg) and t is the live time (s).

The measurement uncertainty is a combined standard one at coverage factor $k = 2$, taking into account the following components: uncertainty counting statistics, uncertainty in nuclear data library, uncertainty due to calibration efficiency, uncertainty about the quantity of the sample, uncertainty due to the correction for self-absorption.

For the dose rate determination, crucial to estimate the radiological risk from external irradiation, conversion coefficients were used, as detailed in the following equation (Ramasamy et al. 2011):

$$D \left(\frac{nGy}{h} \right) = 0.462 C_{Ra} + 0.604 C_{Th} + 0.0417 C_K \tag{2}$$

where C_{Ra} , C_{Th} and C_K are the mean activity concentrations (Bq/kg) of ²²⁶Ra, ²³²Th and ⁴⁰K in the sand samples, respectively (UNSCEAR 2000).

For the determination of the annual effective dose equivalent (AEDE) received by an individual that stays 3 months (in the summer period) in the investigated areas, the conversion coefficient to effective dose 0.7 Sv/Gy and the outdoor occupancy factor of 0.2 were used (Orgun et al. 2007):

$$AEDE \text{ (outdoor)} \left(\frac{mSv}{y} \right) = \text{absorbed dose} \left(\frac{nGy}{h} \right) \times 8760 \text{ h} \times 0.7 \frac{Sv}{Gy} \times 0.2 \times 10^{-6} \tag{3}$$

XRF spectrometry analysis

The elemental composition of the sands from the different locations was performed by XRF spectrometry to determine the chemistry of the rocks in terms of major, minor and trace elements by the method WDXRF with Bruker model S8 Tiger setup (Bruker 2015a).

The excitation source is a tube of Rh at 4 kW. The power and the current intensity are changed according to the analyzed element and its quantity, in order to avoid the detector saturation. The concentrations of the major and minor elements have been calculated through the use of the software package GEO-QUANT M, an accurate method for measuring 11 elements using more than 20 certified material for calculating the calibration lines (Bruker 2015b). For the calculation of the trace elements, however, the software GEO-QUANT T, a simple solution for the determination of these elements in geological materials, was used (Bruker 2015b). The latter is a pre-calibrated and standardized method by the manufacturer, installed in the instrument present in the laboratory. This method is validated using two standard samples GBW07103 and GBW07406 with whom, by performing a quality control, the analysis must meet narrow analytical range provided by the certificates of these standards.

Results and discussion

Radioactivity analysis

The average activity concentration of detected radionuclides, ²²⁶Ra, ²³²Th and ⁴⁰K, in the investigated samples, is reported in Table 1 for the twelve selected locations.

Experimental values are in the range 31–98 Bq/kg for ²²⁶Ra, 14–65 Bq/kg for ²³²Th and 567–932 Bq/kg for ⁴⁰K, respectively. The activity concentration of ⁴⁰K is of about one order of magnitude greater than that of the ²²⁶Ra and ²³²Th, in good agreement with literature (Gupta et al. 2010; Sentilkumar et al. 2010; Caridi et al. 2015). The highest activity concentration of ²²⁶Ra, ²³²Th and ⁴⁰K is found in RC-S. Gregorio, Brancaleone and Roccella J. beaches, respectively. Worldwide average concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K are 35, 30 and 400 Bq/kg, respectively, as reported in literature (UNSCEAR 2000). Our results show that the activity concentration of ²²⁶Ra in our samples is higher than the average world value, except for the Brancaleone beach. The value for ²³²Th is higher than the worldwide one only for Bova M., Brancaleone, Siderno and Roccella J. beaches. The activity concentration of ⁴⁰K is higher than the average world value for all investigated samples.

Table 1 Activity concentration of ^{226}Ra , ^{232}Th , and ^{40}K in the sand samples

Gamma spectrometry results	Sampling site	^{226}Ra (Bq/kg)	^{232}Th (Bq/kg)	^{40}K (Bq/kg)
1	S. Ferdinando	72 ± 14	24 ± 2	878 ± 77
2	Gioia Tauro	95 ± 17	14 ± 1	812 ± 7
3	Palmi	90 ± 15	14 ± 1	923 ± 81
4	Reggio C.-Oasi	87 ± 16	15 ± 1	787 ± 69
5	Reggio C.-Capannina	79 ± 13	28 ± 2	653 ± 57
6	Reggio C.-S. Gregorio	98 ± 17	19 ± 1	629 ± 55
7	Bova M.	67 ± 11	33 ± 2	753 ± 66
8	Palizzi	56 ± 10	27 ± 2	879 ± 77
9	Brancaleone	31 ± 5	65 ± 5	567 ± 50
10	Bovalino	67 ± 12	19 ± 1	783 ± 69
11	Siderno	59 ± 11	31 ± 2	747 ± 66
12	Roccella J.	52 ± 9	36 ± 3	932 ± 82

Evaluation of radiological hazard effects

Absorbed dose rate

Calculated values (nGy/h) of absorbed dose rate are reported in Table 2. They are in the range 75 nGy/h (Bovalino beach)–88 nGy/h (Palmi beach). The average absorbed dose rate for all investigated samples (81 nGy/h) is higher than the average world value (60 nGy/h) (UNSCEAR 2000).

As described before, sand samples in all studied beaches were collected from the spots that showed the highest gamma dose rate determined by in situ measurements. According to (Malanca et al. 1996) usually there is no good agreement between calculated and measured gamma-ray activity. However our results show a high correlation ($R = 0.91$) between these gamma dose rates, as can be seen in Fig. 2, indicating that the field and laboratory

measurements are mutually corroborative. In particular, the in situ gamma dose rate measurements results are in the range 78 nGy/h (Brancaleone beach)–89 nGy/h (Gioia Tauro and Palmi beaches).

The 0.91 factor describes how well the line fits on the points. In this case the situation of the 1:1 line and the function of the linear model is of interest. If the slope of the linear model is very close to that of the 1:1 line, the dose estimation method is appropriate to apply. If the two slopes are similar, it also means that the two methods can be applied well without each other for further similar investigation sites (no need to measure the dose rate because the estimation method provides a good estimation). However, if the slopes are different it means that the dose estimation method has to be reviewed and it can only be applied very carefully. In our case, the two slopes are similar and the 1:1 line falls within the 95 % confidence interval, as reported in Fig. 2. So we can conclude that it is possible to apply the

Table 2 Absorbed dose rate in air and AEDE outdoor in all investigated samples

Gamma spectrometry results	Sampling site	Absorbed dose rate (nGy/h)	Effective dose rate outdoor (mSv/y)
1	S. Ferdinando	85	0.104
2	Gioia Tauro	86	0.106
3	Palmi	88	0.109
4	Reggio C.-Oasi	82	0.101
5	Reggio C.-Capannina	81	0.100
6	Reggio C.-S. Gregorio	83	0.102
7	Bova M.	82	0.101
8	Palizzi	78	0.097
9	Brancaleone	77	0.095
10	Bovalino	75	0.093
11	Siderno	77	0.095
12	Roccella J.	85	0.104

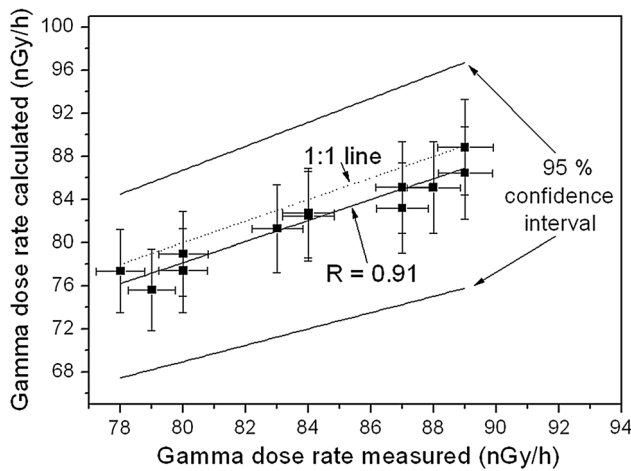


Fig. 2 Correlation between measured and calculated gamma dose rate in the investigated sands

dose estimation method, without measuring the dose rate, as long as the 1:1 line falls within the 95 % confidence interval and for sites with the same geological provenience of the investigated samples (for example other beaches of the coast of Calabria).

The annual effective dose equivalent

Values of the AEDE (mSv/y) for investigated locations are reported in Table 2. They are in the range 93 μSv/y (Bovalino beach)–109 μSv/y (Palmi beach), higher than the world average value of 70 μSv/year (Orgun et al. 2007), but not radiological hazards for the local population. In fact

this range is much lower than the limit set by the Italian legislation (1 mSv/y, D.Lgs. 230/95) and, in any case, comparable to the average environmental background of the places under investigation measured during other campaigns on site.

XRF analysis

XRF analysis results for major and minor elements investigation are reported in Table 3 and shown in Fig. 3. The most abundant elements in all investigated sands are SiO₂ (mean value of 73 %) and Al₂O₃ (mean value of 13 %). The presence of Fe (mean concentration value of 2 % for Fe₂O₃) is also relevant. The mean concentrations of TiO₂ follow the same trend as Fe₂O₃ with lowest mean value (0.3 %). TiO₂ is the most common compound of titanium and is widely distributed in the earth’s crust. The mean concentration of CaO varied from 1 to 4 %, with the highest concentration found in Palizzi and the lowest one in Gioia Tauro. Similarly the concentrations of K₂O and Na₂O varied from 2 to 4 % for the first one and from 2 to 3 % for the second one, respectively. The highest and the lowest concentrations of K₂O were found in S. Ferdinando and RC-S. Gregorio, respectively. The highest and the lowest concentrations of Na₂O were found in Palizzi and RC-Capannina, respectively. Another minor element detected is MgO (mean value of 1 %).

Figure 4 reports TiO₂ (%) as a function of Fe₂O₃ + MgO (%) for all investigated samples (points). These values were compared with a diagram for the tectonic

Table 3 Concentrations of major and minor elements in sand samples

XRF results (major and minor elements)	Sampling site	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	K ₂ O (%)	Na ₂ O (%)	MgO (%)	CaO (%)	TiO ₂ (%)	P ₂ O ₅ (%)	SO ₃ (%)	MnO (%)
1	S. Ferdinando	77	12	0.9	4.2	2.7	0.3	1.6	0.1	0.1	0.02	0.02
2	Gioia Tauro	79	11	1.1	3.3	2.9	0.5	1.2	0.2	0.1	–	0.03
3	Palmi	76	12	1.3	3.7	3.3	0.6	1.3	0.2	0.1	0.01	0.03
4	Reggio C.-Oasi	76	12	1.5	3.6	2.7	0.7	1.8	0.2	0.1	0.02	0.02
5	Reggio C.-Capannina	71	14	3.1	2.6	3.3	1.3	2.1	0.4	0.1	0.03	0.05
6	Reggio C.-S. Gregorio	76	11	1.9	2.3	3.2	0.9	1.9	0.2	0.1	0.02	0.03
7	Bova M.	73	12	2.8	2.8	2.9	1.1	2.4	0.4	0.1	0.06	0.08
8	Palizzi	73	11	2.7	2.9	2.3	1.1	4.1	0.3	0.1	0.04	0.08
9	Brancaleone	73	13	2.9	3.2	2.9	1.4	1.6	0.4	0.1	0.04	0.06
10	Bovalino	76	11	1.7	3.1	2.4	0.7	1.8	0.2	0.1	–	0.06
11	Siderno	74	13	2.4	3.7	2.7	0.9	2.3	0.3	0.1	–	0.05
12	Roccella J.	72	15	2.4	3.5	3.2	0.9	1.2	0.3	0.1	–	0.04

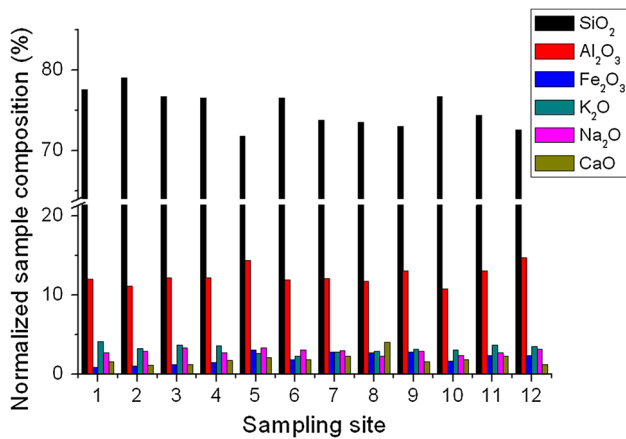


Fig. 3 XRF composition in terms of major and minor elements for all analyzed samples

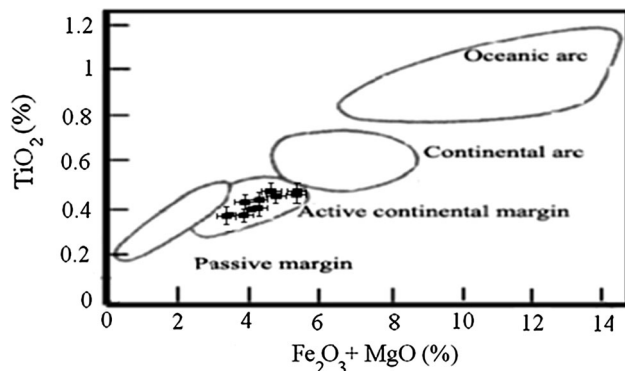


Fig. 4 TiO_2 (%) as a function of $\text{Fe}_2\text{O}_3 + \text{MgO}$ (%) for all investigated samples (points) and a diagram for the tectonic discrimination of sediment provenance

discrimination of sediment provenance, reported in literature (Bhatia 1985).

The comparison puts in evidence that all sands are representative sediments from active continental margins.

Figure 5 reports $\text{Al}_2\text{O}_3/\text{SiO}_2$ (%) as a function of $\text{Fe}_2\text{O}_3 + \text{MgO}$ (%) for all investigated samples (points) and a diagram for the tectonic discrimination of sediment provenance (Bhatia, 1985). A comparison between them puts again in evidence that all sands are sediments from active continental margins.

This comparison with literature was made to determine the geological provenience of the investigated samples and from obtained results we can say that they probably arise from the dismantling and transportation of materials present in the “Calabrian-Peloritan arc” (Atzori et al. 1984).

Its rocks are acidic intrusive igneous (e.g. granites) and metamorphic of medium and high grade (e.g. gneiss). This justifies the presence of SiO_2 , Al_2O_3 and Fe_2O_3 whereas low amounts of CaO , K_2O , Na_2O and MgO are due to their high solubility in water and their low molecular resistance.

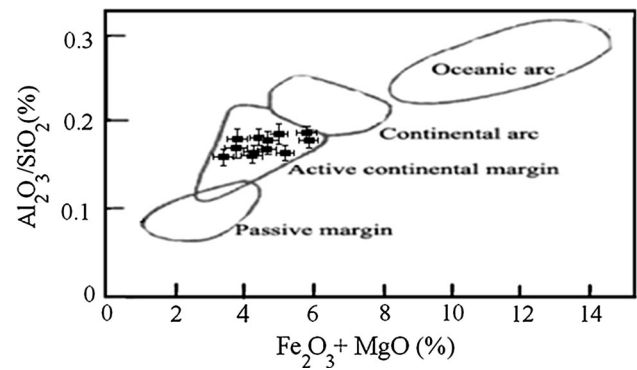


Fig. 5 $\text{Al}_2\text{O}_3/\text{SiO}_2$ (%) as a function of $\text{Fe}_2\text{O}_3 + \text{MgO}$ (%) for all investigated samples (points) and a diagram for the tectonic discrimination of sediment provenance

Conclusions

The activity concentration of natural terrestrial radionuclides ^{226}Ra , ^{232}Th and ^{40}K was measured using HpGe gamma spectrometry for beach sands collected from twelve tourist areas of the coast of Calabria, south of Italy. Reported values are comparable to the average worldwide ranges.

The health risk was evaluated by the absorbed dose rate calculation (in good agreement with that one determined experimentally by in situ measurements, see Fig. 2) and by the annual estimated average effective dose equivalent (AEDE) received by an individual that stays about 3 months (in the summer period) in 1 year in the detected areas. Obtained values are comparable to the world average ones and they are not radiological hazards for the local population because they are much lower than the limit set by the Italian legislation for the population.

XRF analyses were performed to investigate about the elemental composition of all analyzed sands to determine their geological provenience. From obtained results we can establish that these samples come from the dismantling and transportation of materials of the “Calabrian-Peloritan arc”, whose rocks are acidic intrusive igneous and metamorphic, characterized by the highest natural radioactivity. In fact, acid intrusive rocks have, generally, a high uranium content, while that of U and Th in metamorphic rocks depends on the material from which they are derived. Measured activity concentrations of ^{226}Ra are typical of acid igneous and metamorphic rocks and therefore confirm results obtained with the XRF analysis. From these results we can conclude that there are no other types of beach sands which could lead to a higher health risk of exposure.

This study can be used as a baseline for future investigations about radioactivity background levels in beach sands of the coast of Calabria.

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